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# CANADIAN PATENT

LUBRICANTS

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Canada

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The present invention relates to high viscosity lubricants and in particular high viscosity lubricants which may come into contact with aluminium during cold rolling or other cold working process.

It is found that the viscosity of certain high viscosity compositions containing substances of the polyolefin type becomes materially reduced in a relatively short space of time (i.e. within a few hours) when subjected to heavy working conditions under which they are subjected to heavy pressures and shear. This is a very substantial drawback to the use of such compositions as lubricants.

For example it is usual for the manufacturers of rolling mills to specify a minimum viscosity for lubricants for use in the bearings of such equipment. The particular disadvantage of polyolefins in lubricants is that their viscosity is dynamically unstable so that it is difficult to predict the actual viscosity of these compositions under the working conditions to which they would be subjected as lubricants.

On the other hand, polyolefins would have certain advantages for use as lubricants in apparatus performing certain metal working processes on aluminium.

It has already been explained in Patent No. 639255 that if the surface of aluminium bears a film of previously known rolling lubricants it is subjected to severe staining when it is annealed under the most favourable conditions for carrying out the annealing process. Patent No. 639255 discloses rolling lubricants which overcome that problem. However, it has been found in practice that, with many rolling mills, bearing oil tends to seep into the rolling lubricant system.

The conventional roll bearing lubricants are petroleum fractions of a high boiling range, their viscosity depending on their boiling range. They have the advantage for use in rolling mills that their viscosity is dynamically stable, but in mills for the cold rolling

of aluminium they have the disadvantage that they are heavily staining of aluminium, and if such roll bearing lubricants leak into the rolling lubricant to any substantial extent, it can destroy the advantage arising from the use of the new stain-free or low-staining rolling lubricants provided by the use of long-chain, saturated aliphatic alcohols in light petroleum fractions, as described in Patent Specification No. 639255.

It has already been proposed to make rolling lubricants by compounding polybutenes with a light, thermally stable mineral oil, because of the relatively low staining effect of the polybutenes when heated in contact with metal. These rolling oils were of relatively low viscosity and contained only about 1-3% polybutenes of a molecular weight of 50,000-60,000, although the use of up to 30% polybutenes has been suggested.

When a lubricant is compounded from a commercially available polybutene and a light mineral oil to produce a viscous lubricant having a viscosity greater than 600 seconds, Redwood No. 1 at 100°F. its viscosity falls away under an application of shearing forces and becomes permanently reduced within a few hours. Furthermore, heavy loads and shearing forces have an additional temporary effect on the viscosity of these oils in that their viscosity is reduced while the action of the shearing forces and loads takes place and increases again after they cease to operate.

This difficulty can be overcome in a simple way, according to the present invention by the addition of "viscosity stabilizers". These are highly reactive organic substances of low molecular weight such as monomers, dimers, tetramers, etc., which by virtue of a reactive double bond in their molecules can be easily polymerised. The molecular weight of the viscosity stabiliser is preferably below 250 and should not exceed 500. The preferred viscosity stabiliser

additive is propylene tetramer in an amount of 1-3%, but monomers, such as styrene or acrylic acid may be used. The mechanism by which the viscosity stabilizer performs its function is not fully understood, but it is considered that it reacts rapidly with "free radical"-like substances formed temporarily when the polybutene or other polyolefin chain is broken under heavy shearing forces which occur in rolling mill bearings. Since the additive tends, itself to polymerize and since its reaction with the degraded polybutene tends to form compounds of longer chain lengths, it is important that the percentage of the additive incorporated in a lubricant composition should be carefully regulated, so that there is no excessive increase in viscosity as a result. It follows that the percentage of "viscosity stabilizer" additive will be regulated by a number of factors, such as the duty to which the lubricant composition is to be subjected and the molecular weight and type of the polybutene or other polyolefin used in the lubricant composition, and the actual choice of the viscosity stabilizer. When the viscosity stabilizer is one of the substances named above it is preferred to use it in an amount less than 5% and preferably in the range of 1 - 3%.

In considering the use of polybutenes in lubricant compositions for use in the bearings of rolling mills for aluminium the reason why the polybutene composition does not lead to the formation of stains on the aluminium is that, at the temperature of the subsequent annealing state, the polybutenes are readily broken down into short chain molecules which do not stain the aluminium. It will be appreciated that only those polyolefins which break down readily at or below the annealing temperature could be considered as being suitable for use in rolling mill bearing lubricants. At the same time it is desirable that the complexes formed as a result of the addition of the monomer should likewise break down so that they too do not form staining substances. It is not so important for this

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to be the case because the actual amount of such complexes present in the actual rolling lubricant, by reason of leakage of bearing lubricant into it, will be very small and, consequently, their staining effect may in many cases be immaterial.

- 5        The following are examples of lubricants which possess a high original viscosity, retain it after the application of shearing forces, and are free from or have only a small tendency to form brown stains on aluminium strip during annealing under the conditions which may be employed with the rolling lubricant described in Patent No. 639255.
- 10

COMPOSITION 1

Mineral Colza	24%	}	original viscosity 1600 seconds, Redwood No. 1 at 100°F., after the application of shearing forces for 15 hours, 2000 seconds Redwood No. 1 at 100°F.
Polybutene 24	75%		
Styrene	1%		

15

COMPOSITION 2

Mineral Colza	48%	}	original viscosity 1150 seconds Redwood No. 1 at 100°F., after the application of shearing forces for 15 hours, 1350 seconds Redwood No. 1 at 100°F.
Polybutene 128	50%		
Styrene	2%		

COMPOSITION 3

20	Mineral Colza	48%	}	original viscosity 1150 seconds Redwood No. 1 at 100°F., after the application of shearing forces for 15 hours, 1350 seconds Redwood No. 1 at 100°F.
	Polybutene 128	50%		
	Acrylic acid	2%		

COMPOSITION 4

25	Mineral Colza	46%	}	original viscosity 1200 seconds Redwood No. 1 at 100°F., after the application of shearing forces for 15 hours, 1800 seconds Redwood No. 1 at 100°F.
	Polybutene 128	50%		
	Styrene	2%		
	Lauryl alcohol	2%		

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COMPOSITION 5

Polybutene 128	52%	)	original viscosity 1250
Propylene tetramer	2%	)	seconds Redwood No. 1 at
Stearyl alcohol	0.5%	)	100°F., after the appli-
Cetyl alcohol	0.5%	)	cation of shearing forces
Santolube AR }	0.05%	)	for 15 hours, 1475 seconds
Topanol BnT ) anti-	0.1%	)	Redwood No. 1 at 100°F.
oxidants		)	
Gulf Mineral Seal Oil	the balance	)	

10 It was found that by varying the polybutene content of Composition 5 the viscosity could be increased from 175 seconds Redwood No. 1 at 100°F. with 30% polybutene to 1000 seconds Redwood No. 1. at 100°F with 50% polybutene and up to 2790 seconds Redwood No. 1 at 100°F. with 60% polybutene, the polybutene being polybutene 128 in each case. For the present purpose a polybutene content of 45-55% is preferred.

20 Polybutene 24 and polybutene 128 are grades which are sold by Cronite Chemical Company and are stated to have an average approximate molecular weight of 940 and 2700 respectively and viscosities of 40,000 S.S.U. (Seconds Sayboul Universal) and 890,000 S.S.U. respectively at 100°F. It is preferred in the present invention to utilize a polybutene of a molecular weight of less than 5000, as compared with polybutenes of a molecular weight of 50,000 - 60,000 which have been suggested for use in the prior lubricant compositions already referred to.

The Mineral Colza Oil, with which the polybutenes were compounded, is a light petroleum fraction having a very low bromine number, so that it contains very few unsaturated groupings which are believed to lead to some staining problems. Gulf Mineral Seal Oil is another oil having similar characteristics.

30 Using a lubricant with 50% polybutene 128 and other ingredients in the proportions given in Composition 5 excellent protection was given to white metal-steel bearings of a mill for cold-rolling aluminium strip.

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Its leakage into the virtually non-staining cold rolling lubricant did not give rise to any staining tendency of the strip, even when the concentration of the bearing lubricant in the rolling lubricant was allowed to rise to the unusually high level of 15%.

5 It will be observed that in all the above cases the viscosity of the lubricants after a number of hours service was actually increased by virtue of the very small quantity of monomer or low molecular weight reactive polymer additive present. The amount of styrene required to stabilise the lower molecular weight polybutene was less  
10 than that required for the higher molecular weight.

It will readily be appreciated that although other viscosity stabilisers than those named may be used for the present purpose, any other substance used for this purpose must be soluble in the polybutene composition to such extent as to enable it to be maintained  
15 in solution to the extent necessary to effect viscosity stabilisation.

The reason for preferring propylene tetramer to styrene as an additive arises out of the somewhat toxic nature of styrene. On the other hand, propylene tetramer has a slight disadvantage that a polybutene stabilised with it gives rise to slight brown staining  
20 when heated in contact with aluminium, although this staining is negligible when compared with that due to conventional bearing oils.

The staining tendency of polybutene type of bearing lubricant stabilised with propylene tetramer can be largely suppressed by the use of anti-oxidant additives such as 0.1% para-tertiary-butyl  
25 catechol or para-tertiary-butyl phenol.

The purpose of the addition of the long chain saturated fatty alcohols in Compositions 4 and 5 is to act as non-staining load bearing additives when the mill rolls are turning slowly. These fatty alcohols are preferably straight chain and have a chain length  
30 of at least seven carbon atoms. Under slow speed conditions the

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hydrodynamic lubrication due to polybutene is only partially developed and it is therefore found desirable to add up to about 5%, preferably  $\frac{1}{2}$  - 2%, of the load bearing additive to support the load under these conditions.

5        The purpose of the addition of antioxidants, such as Santolube AR and Topanol BHT (Composition 5), is to prevent the development of acidity in the roll bearing lubricants. It is known to be important that the rolling oil of the composition explained in Patent No.639255 should be free from acidity and hence it is also important  
10       that any bearing oil which leaks into it should not be acidic. Polybutenes in a petroleum fraction tend to develop acidity during service, but this difficulty can be obviated by an addition of a suitable antioxidant. The actual choice of the antioxidant depends on the grade of polybutene, on the type of petroleum fraction and on  
15       the viscosity stabiliser used. Topanol BHT and Santolube AR are only two of many antioxidants that could be used.

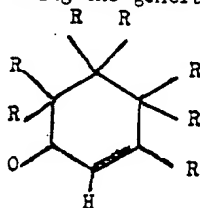
When a lubricating composition of the present type was tested in a foil-bearing apparatus, it was found that the lubricant behaved as a non-Newtonian fluid with a coefficient of friction increasing  
20       with increasing rate of shear in the region of mixed friction in which it was designed to operate. The results obtained indicated that the lubricant composition was superior to the Newtonian mineral oils of comparable viscosity which are in standard general use.

All proportions hereinabove given are proportions by volume.

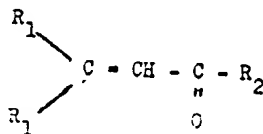
SUPPLEMENTARY DISCLOSURE

Subject to the qualification of a maximum molecular weight of 500 previously stated and preferably subject to a maximum molecular weight of 250 it appears that all oil-soluble olefinically unsaturated carboxylic acids, esters, aldehydes, suitable as viscosity stabilizers, but these should not, for preference, contain substituents, such as halogens or sulphur or nitrogen-containing groups. The preferred viscosity stabilizer additive is, as already disclosed, propylene tetramer in an amount of 1-3%, but many other alkenes (either monomer or lower polymer) are suitable. However, straight chain olefinic compounds, such as n-decene, are unsuitable. Other reactive unsaturated substances such as mesityl oxide or iso-phorone may be used. Other suitable viscosity stabilizing additives include acrolein, crotonaldehyde, vinyl acetate, methacrylic acid, methyl methacrylate and methyl acrylate and other lower alkyl esters of acrylic acid and methacrylic acid.

Examples of other substances suitable for use as viscosity stabilizers are those having the general formula

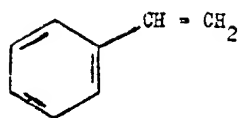


in which R may be hydrogen, lower alkyl or acyl groups



in which  $R_1$  may be hydrogen, lower alkyl or aryl groups and in which  $R_2$  may be hydrogen lower alkyl or aryl groups

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in which the nucleus may be substituted at one or more positions with alkyl or acyl groups.

It is preferable that the bromine number of the compounded lubricant composition, including the viscosity stabilizer, should not exceed 6 and in any event must not exceed 25.

In order to test the stabilising effects of other unsaturated substances on the viscosity of polybutenes a composition was made up comprising 58.8% polybutene 128 and 39.2% odourless kerosene (boiling range 203-259°C. bromine number 0.25 and viscosity 30 SSU at 100°F.).

To this was added 2% of the substances listed below and the composition was then subjected to shearing forces in an ultrasonic testing machine for 10 minutes.

Substance	Initial viscosity SSU at 100°F.	Final viscosity SSU at 100°F.
Methyl methacrylate	1150	1200
Crotonaldehyde	1160	1205
Dipentene	1157	1208
Vinyl Acetate monomer	1100	1120
Polybutene light polymer (Mixture of butylene tetramer and pentamer in 1:1 ratio)	1200	1200
Acrylic acid	1170	1168
Methyl acrylate	1100	1108
Iso-phorone	1150	1175
Mesityl oxide	1130	1140
Kerosene (control)	1160	850

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It will be seen that with those substances which increase the viscosity of the composition under test the amount used for accurate viscosity stabilization should be less than 2%.

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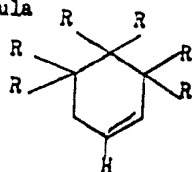
All proportions hereinabove given are proportions by volume.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A high viscosity lubricant composition having a viscosity in excess of 600 seconds Redwood No. 1 at 100°F comprising a polybutene and a viscosity stabilizing additive, consisting of an organic substance of a molecular weight below 500 containing a reactive double bond and a light mineral base oil having a low bromine number.
2. A composition as claimed in claim 1 in which the stabilizer has a molecular weight less than 250.
3. A composition as claimed in claim 1 in which the polybutene has a molecular weight of less than 5000.
4. A composition as claimed in claim 1, 2 or 3 comprising 30-60% polybutene, less than 5% of a viscosity stabilizer selected from propylene tetramer styrene and acrylic acid, the balance being a light mineral base oil.
5. A composition according to claim 1 wherein the polybutene has a molecular weight of about 2500.
6. A composition according to claim 1, 2 or 3 wherein the viscosity stabilizer comprises 1-3% of propylene tetramer.
7. A composition according to claim 3 or 4 wherein the polybutene is present in the range of 45-55%.
8. A composition according to claim 1, 2 or 3 further including up to 5% of long-chain saturated fatty alcohol as a load bearing constituent.

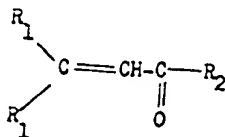
CLAIMS SUPPORTED BY THE SUPPLEMENTARY DISCLOSURE

9. A composition as claimed in claim 1 in which the mineral oil has a bromine number below 25.
10. A composition as claimed in claim 1 in which the mineral oil has a bromine number below 6.
11. A composition as claimed in claim 1 in which the stabilizer has a molecular weight below 300.
12. A composition as claimed in claim 9, 10 or 11 in which the viscosity stabilizer is the compound of the formula



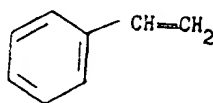
where R is hydrogen or a lower alkyl or acyl group.

13. A composition as claimed in claim 9, 10 or 11 in which the viscosity stabilizer is a compound of the formula



wherein  $R_1$  and  $R_2$  are the same or different and represent hydrogen, lower alkyl or aryl.

14. A composition as claimed in claim 9, 10 or 11 in which the viscosity stabilizer is a compound of the formula



in which the benzene nucleus is unsubstituted or substituted in one or more positions by alkyl or acyl groups.

15. A composition as claimed in claim 9, 10 or 11 in which the viscosity stabilizer is methyl methacrylate, crotonaldehyde, dipentene, vinyl acetate

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monomer, acrylic acid, methyl acrylate, mesityl oxide, iso-phorone or a poly-butene light polymer which is a mixture of a butylene tetramer and pentamer in a 1:1 ratio.